Preparation, chiroptical properties and their computational analysis, of some camphor benzocyclotrimers.

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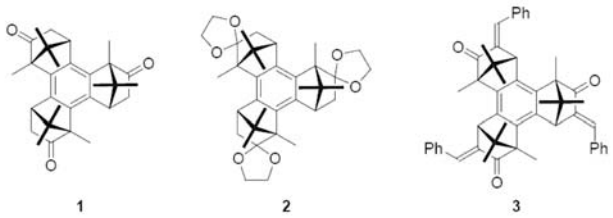
The large molecules 1-3 (69, 90 and 102 atoms), prepared by cyclotrimerization of enantiomerically pure derivatives of (-)-bornyl acetate,1 show intense ECD spectra, high OR values (200/1300, in absolute value) dominated in sign and order of magnitude by the lowest-energy Cotton effects, i.e. they are the ideal candidates to test the reliability of our "approximate"(TDDFT/B3LYP/6-31G* or smaller basis set) approach [2] to the calculation of chiroptical properties. As a matter of fact, a correct simulation of the OR values and ECD spectra of 1 and 2 can be obtained even using STO- 3G basis set and semiempirical ot molecular mechanics input geometries: for 1, at the TDDFT/B3LYP/STO-3G level, the OR values are of the order of 500-550, versus an experimental value ranging between 660 and 690, depending on the solvent. On the contrary, the case of 3 (exp. OR between -1330 and -1500) is really complex (for instance, the OR values range between –3216 and -729 (TDDFT/B3LYP/6-31G* calculations) or -1824 and -444 (TDDFT/B3LYP/STO-3G calculations)), making the comparison between calculated and experimental values more difficult. We have shown that this is due to the molecular flexibility, i.e. in 3 there is (almost) free rotation around the single bond connecting the benzene ring to the double bond, so the theoretical structure we use as input geometry for the OR and ECD calculations may depend on the optimization technique employed, making more difficult the comparison between experimental and theoretical values. On the contrary, 1 and 2 are really rigid molecules. These observations strongly indicate that the conformational freedom constitutes one of the major difficulties for a correct but simple simulation of the chiroptical properties.



1 2 3

References and notes

1. Scarso, A.; Pellizzaro, L.; De Lucchi, O.; Linden, A.; Fabris, F. Angew. Chem. Int. Ed. 2007, 46, 4972-4975.

2. Giorgio, E.; Minichino, C.; Viglione, R. G.; Zanasi, R.; Rosini, C. J. Org. Chem. 2003, 68, 5186-5192.